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Elevated levels of aluminum in acidic surface waters have been attributed to the dissolution of soil minerals by acidic atmospheric deposition. There is currently considerable interest in aqueous chemistry of aluminum because of its role, a) as a toxicant to aquatic organisms, b) in the cycling of orthophosphate and organic carbon, and c) as a pH buffer. In this study we evaluated the chemistry of aluminum in an acidic drainage lake.

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# THE CHEMISTRY OF ALUMINUM IN AN ACIDIC LAKE IN THE ADIRONDACK REGION OF NEW YORK STATE, USA

C.T. DRISCOLL and G.C. SCHAFRAN

## 1. INTRODUCTION

Elevated levels of aluminum in acidic surface waters have been attributed to the dissolution of soil minerals by acidic atmospheric deposition (Dickson, 1978; Johnson et al., 1981). There is currently considerable interest in aqueous chemistry of aluminum because of its role, a) as a toxicant to aquatic organisms (Baker and Schofield 1982), b) in the cycling of orthophosphate and organic carbon (Dickson, 1978), and c) as a pH buffer (Dickson, 1978; Driscoll and Bisogni, 1984). In this study we evaluated the chemistry of aluminum in an acidic drainage lake.

## 2. STUDY SITE AND METHODS

The study site, Dart Lake, is located in the Adirondack region of New York State, U.S.A. (74°52'W, 43°48'N). Samples were collected for water quality analysis at the inlet, outlet and at seven depths from a pelagic sampling station approximately every two weeks over an annual cycle (10/25/1981-11/21/82).

Aqueous aluminum was fractionated into labile monomeric aluminum (IMAl), non-labile monomeric aluminum (OMAl) and acid soluble aluminum (ASAl) (Driscoll, 1984) and detected using the procedure of Barnes (1975). Water samples were analyzed for all major solutes using standard methods (Driscoll and Schafran, 1984). Thermodynamic calculations used in this study were made with a modified version of the chemical equilibrium model MINEQL (Westall et al., 1976). The thermochemical data used in our calculations are summarized elsewhere (Driscoll, 1984). To evaluate the distribution of IMAL we calculated aquo aluminum ($Al^{3+}$), hydroxide (Al-OH), fluoride (Al-F), sulfate ($Al\text{-}SO_4$) complexes of aluminum and

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aluminum base neutralizing capacity (Al-BNC; Table 1). We define hydrogen ion and aluminum base neutralizing capacity (H-Al-BNC) as the amount of strong base required to increase the pH of a liter of aluminum solution to 8.3. Further details on the study site, research program and analytical methods are available elsewhere (Driscoll and Schafran, 1984).

## 3. RESULTS AND DISCUSSION

Like many other investigators (Dickson, 1978; Johnson et al., 1981; Driscoll et al., 1984), we observed an exponential increase in aluminum, and particularly IMAl, with decreases in solution pH. Variations in hydrogen ion and aluminum BNC were strongly correlated to changes in $NO_3^-$ concentrations ($H\text{-Al-BNC}=0.94(NO_3^-) + 2.4$; in meq $m^{-3}$, $r^2 = 0.54$, $p < 0.0001$). Note that this correlation is linear with a slope close to one and an intercept near the origin. Although $SO_4^{2-}$ was the dominant anion in Dart Lake, no statistically significant relationship with H-Al-BNC was observed. H-Al-BNC was positively correlated with organic anion concentration ($H\text{-Al-BNC} = 33.1(RCOO^-) - 478$; where $RCOO^-$ represents organic anion concentration in meq·$m^{-3}$, $r^2 = 0.13$, $p < 0.0001$) and no statistically significant relationship was observed with $Cl^-$.

Table 1 FORMS OF INORGANIC ALUMINUM AND BASE NEUTRALIZING CAPACITY

| | |
|---|---|
| Aquo aluminum; | $Al^{3+} = [Al^{3+}]$ |
| Hydroxide bound aluminum; | $Al\text{-}OH = [Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_4^-]$ |
| Fluoride bound aluminum; | $Al\text{-}F = [AlF^{2+}] + [AlF_2^+] + [AlF_3] + [AlF_4^-] + [AlF_5^{2-}] + [AlF_6^{3-}]$ |
| Sulfate bound aluminum; | $Al\text{-}SO_4 = [AlSO_4^+] + [Al(SO_4)_2^-]$ |
| Aluminum base neutralizing capacity; | $Al\text{-}BNC = 3[Al^{3+}] + 2[Al(OH)^{2+}] + [Al(OH)_2^+] + 3[Al\text{-}F] + 3[Al\text{-}SO_4] - [Al(OH)_4^-]$ |
| Hydrogen ion and aluminum base neutralizing capacity; | $H\text{-}Al\text{-}BNC = Al\text{-}BNC + [H^+] - [OH^-]$ |

During high flow conditions associated with snowmelt, elevated levels of $NO_3^-$, hydrogen ion and aluminum were introduced to Dart Lake through drainage water. Under these acidic conditions, aqueous aluminum was extremely conservative and transported through the lake with minimal retention. During periods of stratification, microbially mediated assimilation of nitrate served to neutralize H-Al-BNC, resulting in the formation of particulate aluminum

which was deposited to lake sediments. Thus, transformations of nitrate were extremely important in regulating short-term changes in the H-Al-BNC of Dart Lake.

In Dart Lake, fluoride and organic complexes were the predominant forms of aqueous aluminum (Table 2). $Al^{3+}$, Al-OH and ASAl were present at lower but significant levels, while Al-$SO_4$ was insignificant. The concentrations and relative distribution in Dart Lake were similar to values reported by Johnson et al. (1981) for a stream in the Hubbard Brook Experimental Forest (HBEF) in New Hampshire and by Driscoll et al. (1984) for Adirondack surface waters.

In Dart Lake a substantial portion of mononuclear aluminum appeared to be complexed with organic ligands. We observed a weak but statistically significant empirical relationship between OMAl and dissolved organic carbon concentration (OMAl = 0.018 DOC + 1.84, in $mmol \cdot m^{-3}$, $r^2 = 0.14$, $p < 0.0001$). Similar empirical relationships have been reported by Driscoll et al. (1984) for Adirondack lakes and streams and by Driscoll (1984) for HBEF streams.

Table 2 MEAN CONCENTRATION AND STANDARD DEVIATION OF ALUMINUM (in $mmol \cdot m^{-3}$) AND RELATIVE DISTRIBUTION AS TOTAL AND MONOMERIC ALUMINUM

| Aluminum Form | Concentration | Relative Distribution as Total Aluminum | Relative Distribution as Monomeric Aluminum |
|---|---|---|---|
| Total Aluminum (TAl) | 14.8 ± 4.4 | — | — |
| Monomeric Aluminum (MAl) | 11.5 ± 3.7 | 0.78 | — |
| Labile Monomeric Aluminum (IMAl) | 8.1 ± 3.2 | 0.54 | 0.70 |
| $Al^{3+}$ | 1.9 ± 1.7 | 0.13 | 0.17 |
| Al-OH | 2.5 ± 1.3 | 0.17 | 0.22 |
| Al-F | 3.6 ± 0.7 | 0.24 | 0.31 |
| Al-$SO_4$ | 0.1 ± 0.1 | 0.01 | 0.01 |
| Non-labile Monomeric Aluminum (OMAl) | 3.5 ± 0.1 | 0.24 | 0.30 |
| Acid Soluble Aluminum (ASAl) | 3.1 ± 2.1 | 0.22 | — |

The correlation between OMAl and DOC was considerably weaker for Dart Lake than these other systems, which may be attributed in part to the limited

range of DOC (220 - 420 $mmol \cdot m^{-3}$) in our study. Also DOC is a relatively coarse parameter because it encompasses a variety of organic solutes which vary greatly in capacity to complex aluminum.

The toxicity of aluminum to fish is very dependent on the speciation of aluminum (Baker and Schofield, 1982). Moreover the non-conservative nature of aluminum, which was particularly pronounced in Dart Lake during stratification, may influence the cycling of critical nutrients like phosphorus and organic carbon in acidic lake systems. Therefore any assessment of the effects of aluminum in acidic lakes should be made with an understanding of the speciation and transport of aluminum.

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